Experimental studies of the vapor phase nucleation of refractory compounds. IV. The condensation of magnesium

Frank T. Ferguson[a)] and J. A. Nuth III
Code 691, NASA-Goddard Space Flight Center, Greenbelt, Maryland 20771

L. U. Lilleleht
Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22903

Magnesium nucleation was studied over the range of approximately 700 to 950 K in a gas evaporation apparatus. Measured supersaturation ratios ranged from approximately 37 to 4.2 over this temperature range, respectively. A comparison of these data and Classical Nucleation Theory shows that the two are not consistent. Although there is a good correlation between the supersaturation and the temperature data when plotted in accordance with Scaled Nucleation Theory, some of the derived parameters are slightly below the limits predicted by the theory. © *1996 American Institute of Physics.* [S0021-9606(96)02808-5]

I. INTRODUCTION

Interstellar dust grains represent only a small fraction of the total mass within the interstellar medium, yet they play an extremely important role in the chemical and physical evolution of this region. These small grains serve as sites for many chemical reactions and it is widely accepted that molecular hydrogen is formed on the surfaces of these grains. Dust grains absorb and reemit light and are in fact responsible for 30% of the total luminosity of the galaxy.[1] Dust grains may also serve as sites to ''cool'' energetic gas molecules and influence how interstellar gas clouds collapse to form stars. The exact composition of these grains is unknown; major constituents of these grains are believed to be refractory materials such as graphite and metal silicates. These refractory particles are formed from the gaseous ejecta of stars, but the mechanism and conditions under which these particles form are poorly understood.

Only a handful of refractory nucleation studies have been published to date. This lack of data may be due to the difficulty involved in producing and controlling supersaturated vapors of these species. These studies have been performed using one of three different methods: (1) the shock tube technique,[2,3] (2) the gas evaporation technique,[4,5] and (3) the upward thermal diffusion cloud chamber.[6] Almost none of the refractory nucleation data collected to date follows the predictions of the Classical Nucleation Theory[7] or its modifications such as that by Lothe and Pound.[8,9] A recent study of cesium nucleation using an upward thermal diffusion chamber is the only study which has produced experimental refractory nucleation data in agreement with Classical Nucleation Theory.[6] This agreement is also restricted to the higher temperatures of the study—at lower temperatures a larger supersaturation than that predicted by Classical Nucleation Theory is observed. In general, the agreement between Classical Theory and refractory data is very poor and it appears that the Classical Nucleation Theory does not hold for

refractory nucleation experiments which are characterized by high particle fluxes, J, high supersaturations, S, and small critical cluster sizes, n_{cr}^2.

In 1986, Barbara Hale published a Scaled Nucleation Theory which utilizes critical point quantities to write the equations for nucleation in a material independent form.[10] For a flux of 1 $cm^{-3}s^{-1}$, this model predicts the following relationship between the critical supersaturation ratio, S_{cr}, and the condensation temperature, T, for temperatures well below the critical temperature of the material:

$$\ln S_{cr} \approx \Gamma \Omega^{3/2} \left[\frac{T_c}{T} - 1 \right]^{3/2}. \tag{1}$$

The quantity Ω denotes the negative partial derivative with respect to temperature of the surface tension per molecule and typically ranges from 1.5 to 2.2—for most substances Ω has a value of approximately 2.0. T_c is the critical temperature of the material, and Γ is a weak function of the temperature and supersaturation, approximately equal to 0.53. For fluxes larger than 1 $cm^{-3}s^{-1}$, the critical supersaturation is modified as follows:

$$\ln S \approx \ln S_{cr} \left[1 + \frac{\ln J}{(2 \ln J_{cr})} \right] = \ln S_{cr} \cdot Q, \tag{2}$$

where the term $\ln(J_{cr})$ is equal to 72 $\pm$ 3 and Q represents the bracketed term.

Scaled Nucleation Theory has been applied to a wide range of volatile materials with great success. In 1989, Hale *et al.* first tried to apply Scaled Nucleation Theory to refractory nucleation data on silver and SiO (Ref. 11) taken by Nuth *et al.*[4,5] Although the critical temperatures of these materials are not known, Eq. (1) can be rearranged such that a plot of $(\ln S)^{2/3}$ vs $1/T$ yields a straight line. Furthermore, the ratio of the slope of these data to the negative of the intercept provides a method of predicting the material's critical temperature from valid nucleation data. Straightforward application of the published data to the theory yielded unreasonable results and prompted Hale *et al.* to re-examine the original data.

In their original work, Nuth *et al.* derived nucleation temperatures by performing calibration runs with an empty furnace. Thermocouples were placed in the crucible, at the typical position of nucleation and at various other positions around the crucible. These temperatures were recorded over the normal operating range. During an actual run the thermocouples in the nucleation region were removed and the calibration runs were used to predict the temperature at the site of nucleation when the refractory material was placed in the furnace. Nuth *et al.* assumed that the vapor concentration was controlled by the radial diffusion of the vapor away from the crucible source. To determine the condensing concentration they applied a $1/r^2$ dilution factor to the refractory vapor based on the distance of the smoke front away from the crucible. This dilution factor was typically on the order of 1/16. Hale *et al.* reasoned that the temperature measurements should be correct, but it was likely that the refractory metal would be entrained in a buoyant plume above the crucible. If so, the refractory concentration profile would not be diffusion-controlled but should in fact be relatively unchanged from that of the source. After reanalyzing the data under the assumption that the vapor concentration at the condensation point was equal to that of the source, Hale *et al.* found that Scaled Nucleation Theory and the data for silver and SiO were in remarkably close agreement and that the theory predicted rather reasonable critical temperatures for both materials. Unfortunately, an examination of all other refractory nucleation data shows that only these two systems are in strict agreement with Scaled Nucleation Theory.[9]

II. EXPERIMENT

The primary objective of this work is to provide additional data of better quality on the nucleation of refractory species. Another goal is to compare these data with both Classical Nucleation Theory and Hale's Scaled Nucleation Theory. Magnesium was chosen for this experiment because of its relatively low melting point and high vapor pressure. Other materials which we intend to study are zinc, bismuth, lead, and tin.

The experimental apparatus is similar to the system used by Nuth *et al.* to study silver and SiO nucleation and a cross-sectional diagram of the apparatus is shown in Fig. 1. The apparatus consists of a 150 liter stainless steel bell jar which is connected to a valve manifold and set of mechanical and diffusion pumps. The material is vaporized from within an alumina crucible which is surrounded by a resistive heater basket made of tungsten. The temperature at the top of the crucible is measured with a type-K thermocouple and the condensing smoke cloud is illuminated using a xenon arc lamp. A cross section of the smoke plume can also be illuminated using a two-dimensional fan of laser light. This fan of laser light is generated at the port opposite the arc lamp by directing a He–Ne laser at a rotating, polygon-shaped mirror. During an experiment, the furnace and resulting smoke cloud are captured on videotape by a camera mounted on a port at 90° to the arc lamp.

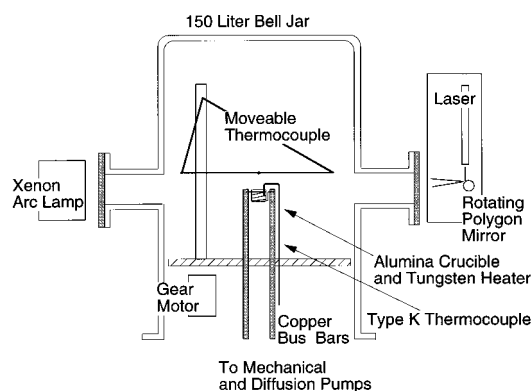There are two significant changes in the apparatus com-

FIG. 1. Cross-sectional diagram of the experimental apparatus.

pared to the system used by Nuth *et al.*, both of which take advantage of the fact that the vapor is constrained to a buoyant plume above the crucible. First, the outer furnace used in Nuth's original system has been removed. Its original role was to establish a conductive temperature gradient and allow some measure of control over the nucleation temperature. Without this outer furnace there is a much wider field of view and we are able to maintain clear, unobstructed sight of the refractory smoke plume. The plume is very strong and steady and condensation typically occurs approximately 1 cm above the crucible top. In fact, this smoke plume is so strong that it prompted us to make the second change in the apparatus. Previously, the temperature at the point of nucleation was calculated via calibration runs made with an empty crucible. In this work the temperature at the smoke-vapor interface is probed directly using a small, thin-wire thermocouple. A diagram of this thermocouple assembly is shown in Fig. 2.

Two lengths of rod are used to suspend the leads of a 0.5mm (0.02 in.) diameter thermocouple over the crucible. Stretching the thermocouple in this manner provides a minimum amount of disturbance to the smoke plume and increases accuracy in junction placement. The length of these two leads can be adjusted such that the junction can be positioned directly over the center of the crucible. In addition,
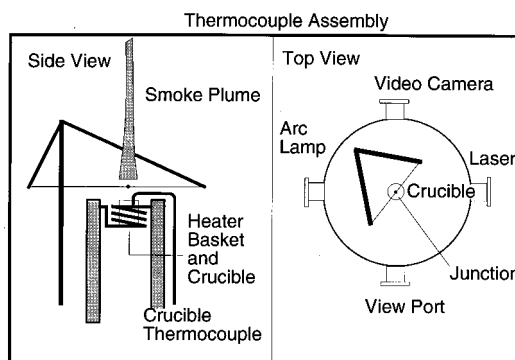

FIG. 2. Thermocouple assembly.

TABLE I. Equilibrium vapor pressure equation constants.

A_v	B_v	C_v	T(K) Range
7780	11.41	−0.855	$298 - T_{mp}$
7550	12.79	−1.41	$T_{mp} - T_{bp}$

the entire thermocouple support assembly is mounted on a gear-driven motor and can be accurately moved up or down above the crucible to follow the moving smoke-vapor interface. In the experiments we have performed the smoke plume is very steady and the presence of this thin thermocouple does not appear to affect the plume or alter the position of the smoke-vapor interface.

During a typical experiment, the apparatus is cleaned and the crucible is filled with pieces of magnesium cut from a solid rod of the material. Before the rod is cut, the surface is ground slightly to remove any oxide coating that may be present on the surface of the rod. After filling the crucible, the chamber is evacuated. One to two hours before a run and while still under vacuum, the crucible is heated to approximately 150 °C. The chamber is then filled with a low to moderate pressure of hydrogen and heating is increased until the first appearance of magnesium smoke. The moving thermocouple is then lowered to the smoke cloud interface. During the run the position of the moving thermocouple is manually adjusted to track the position of the interface and this temperature and the temperature of the crucible are recorded as the crucible is slowly heated and then cooled.

III. RESULTS

A. Nucleation data

There are several assumptions made in this work which should be noted before proceeding. First, it is assumed that the thermocouple used to probe the vapor/smoke interface does not significantly influence the condensation process. In the experiments performed to date, the condensation front is extremely distinct and appears to be unaffected by the movement of the thermocouple through this interface. Second, it is assumed that the thermal convective currents are sufficiently strong within the chamber to keep the refractory vapor constrained within a buoyant plume and essentially undiluted from its source. The flux of particles is assumed to be essentially constant over the temperature range studied and we do not make any corrections to the data for the heat of condensation of magnesium since we measure the temperature of the gas at the point of nucleation directly.

The temperature at the crucible source is also measured directly using chromel-alumel thermocouples. Both the equilibrium vapor pressure at the source and at the condensation point are calculated based on published magnesium vapor pressure data,[12] e.g.:

$$\log P_v = -\frac{A_v}{T} + B_v + C_v \log T, \qquad (3)$$

where the equilibrium vapor pressure equation constants are as given in Table I. The assumption that the vapor concen-
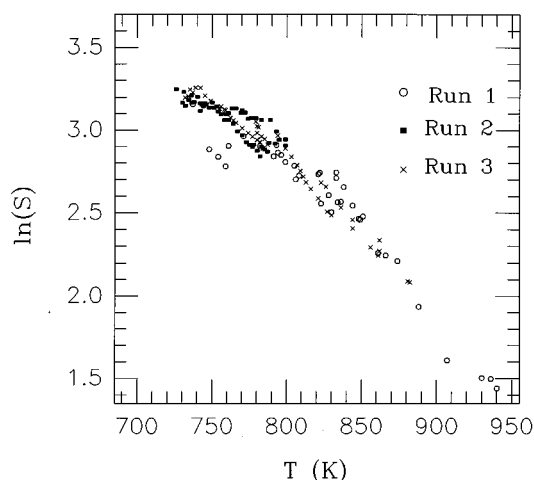
FIG. 3. ln(S) vs T for magnesium at 100 Torr ambient pressure.

tration is not significantly diluted is supported by the fact that the diameter of the rising smoke plume is approximately equal to the diameter of the crucible opening.

Data for magnesium condensation was taken at 100 Torr ambient pressure of hydrogen. This experiment was performed three times to check for repeatability. The results of each of these three runs is shown in Fig. 3. There is considerable scatter in the data, yet the results of each run are consistent. Much of the scatter is due to the fact that the temperature gradient is very steep near the crucible, although there does not seem to be a large temperature drop across the vapor/smoke interface.

Data for magnesium nucleation covers the range from 725 K to 940 K. Supersaturation values range from approximately 26 at the lowest temperature to 4.3 at the highest temperature. Figure 4 is a plot of two additional magnesium condensation runs made at 250 Torr of hydrogen. These results are essentially identical to those at 100 Torr.
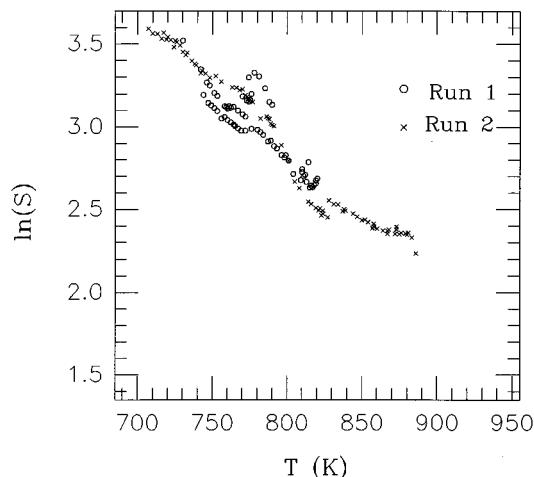
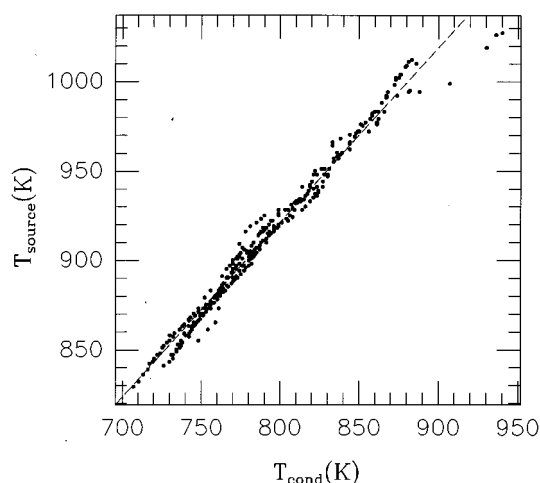FIG. 4. ln(S) vs T for magnesium at 250 Torr ambient pressure.

FIG. 5. Plot of the raw experimental temperature data.

FIG. 6. Plot of $(\ln S)^{2/3}$ vs $1/T$ in accordance with Scaled Nucleation Theory.

The nucleation results presented in this work are very dependent upon the magnesium vapor pressure equation used to reduce the raw data. Because of the sensitivity of our results to this equation, we have decided to publish the raw experimental data, thereby allowing other researchers to re-calculate our results using an updated vapor pressure relationship when or if it becomes available. Because of the volume of experimental data, the results are not tabulated but are instead plotted in Fig. 5. In this plot, the temperature of the crucible source is plotted as a function of the temperature of the magnesium condensation front. As seen from the plot, the data fit a straight line rather well. The equation for this line is

$$T_{\text{source}} = 0.977 \cdot T_{\text{cond}} + 139.4 \tag{4}$$

with an $r^2 = 0.981$. This fit is valid for condensation temperatures ranging from 710K to 890K.

B. Comparison with classical nucleation theory

Classical Nucleation Theory predicts the following relationship for the condensation flux, J:

$$J = \left(\frac{2\sigma}{\pi m}\right)^{1/2} V N_1^2 \exp\left[\frac{-16\pi\sigma^3 V^2}{3k^3 T^3 (\ln S)^2}\right], \tag{5}$$

where σ is the surface free energy, m is the mass of the condensing molecule, V is the volume of the condensing molecule, N_1 is the number density of the monomer, and k is Boltzmann's constant.

Using a melting point literature value of (556 erg cm^{-2})[13] for the magnesium surface free energy and the data collected in this work, Eq. (5) yields an average flux of 10^{-39} cm^{-3} s^{-1} and a maximum flux of only 10^{-37} cm^{-3} s^{-1}. A check on possible errors indicates that a realistic value for the flux is well beyond reasonable limits/assumptions in our data and data reduction.

For example, to obtain fluxes near 10^8 cm^{-3} s^{-1} using Eq. (5) it would require errors of 50–100 °C in our direct thermocouple measurements or vapor pressures 15 times
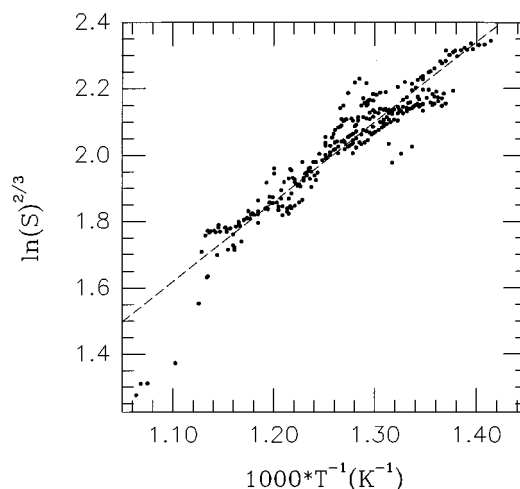
higher than predicted by equilibrium relationships. A some-what lower value of the surface free energy would bring the Classical theory and our data closer in agreement. However, since most of the condensation temperatures fall below the melting point and the solid magnesium would presumably have a higher surface free energy than the liquid, this would tend to widen the gap between our data and classical theory.

C. Comparison with scaled nucleation theory

Scaled Nucleation Theory predicts a linear relationship between $(\ln S)^{2/3}$ and $1/T$. Furthermore, this theory predicts that the ratio of the slope of such a line to the negative of the intercept should be the critical temperature of the material. Fig. 6 is such a plot for the magnesium data collected in our experiments. A least squares linear fit through the data yields

$$(\ln S)^{2/3} = 2405/T - 1.026 \tag{6}$$

with an r^2 of 0.89. This linear fit through the data yields a critical temperature for magnesium of 2343 K. This is very close to the "rule of thumb" estimate of $T_{bp}/0.6 = 2270$ K and is a very encouraging result.

In this work the nucleation flux is not measured, but it is estimated to be $\sim 10^{10}$ particles per cm^3 s^{-1}. Using this estimate and our experimental magnesium data, the critical cluster size can be calculated. According to Scaled Nucleation Theory, the critical cluster size, n_{cr}, is

$$n_{\text{cr}} = \left[\frac{2A}{3B}\right]^3, \tag{7}$$

where

$$A = (36\pi)^{1/3} \Omega \left[\frac{T_c}{T} - 1\right] \tag{8}$$

and

$$B = \ln S. \tag{9}$$

TABLE II. Summary of evaporation experimental results.

Run #	Avg. Temp (°C)	Avg. Press. (Torr)	Mass Loss (g)	Elapsed Time (s)	Mg Vapor Press. (Torr)	Eq. Vap. Press. (Torr)	Ratio
1	628	103	0.1394	3060	0.926	1.78	0.520
2	630	100	0.7253	14400	1.03	1.86	0.554
3	721	99	1.0203	4500	4.88	9.31	0.524
4	630	245	0.4885	15300	0.655	1.86	0.352

Assuming a constant Γ of 0.53 and a flux of 10^{10}, Eqs. (1), (2), and (6) give $\Omega = 1.42$. This value is smaller than expected for a solid—it is closer to that of associated liquids for which $\Omega \sim 1.5$. Eq. (7) predicts a critical cluster size of 28 to 109 magnesium atoms over the temperature range studied in this work.

One reason Scaled Nucleation Theory may provide better agreement between data and theory is that by using scaled quantities, Scaled Theory is able to extend the useful range of Classical Theory. As was pointed out in an earlier paper,[11] quantities like the bulk liquid surface tension and bulk liquid number density, ρ, do not explicitly appear in Scaled Theory—rather they appear as ratios such as

$$\frac{\sigma}{k/\rho^{2/3}} = \Omega[T_c - T] \tag{10}$$

and are replaced in the scaled formalism with the quantity Ω. If the bulk liquid density value is used for ρ in Eq. (10), the *effective* surface energy can be calculated as

$$\sigma = 530.7 - 0.2265T. \tag{11}$$

Equation 11 predicts an effective surface tension of 322 erg cm^{-2} for magnesium at the melting point. This is lower than the literature value of 556 erg cm^{-2}, but it should be noted that the surface tension derived via Eq. (10) may not necessarily correspond with the actual surface tension. It is interesting to note, however, that if Eq. (10) is used for the bulk surface tension in the Classical expression for the flux, the data collected in this work yield reasonable results for the condensation flux, i.e., $J \sim 10^6$ cm^{-3} s^{-1}. In general, the predictions of Scaled Nucleation Theory seem rather reasonable.

Unfortunately, the data and theory are not completely consistent because of the somewhat lower than expected value of Ω. According to Scaled Theory the intercept of Fig. 6 should equal $-(\Gamma Q)^{2/3}\Omega$. In this work the symbol Q is used to denote the term in brackets of Eq. (2) and is a slight correction to the relationship between the supersaturation and the condensation temperature for fluxes higher than 1 cm^{-3} s^{-1}. The values of Q range from 1.13 to 1.29 for fluxes of 10^8 to 10^{18} cm^{-3} s^{-1}—values which are typically found in refractory nucleation studies. The possible range of Ω is therefore 1.5 to about 2.2. This leads to upper and lower bounds for the intercept of -1.71 to -1.06. The intercept derived in this work (-1.026) is slightly larger than that predicted by Scaled Nucleation Theory.

D. Equilibrium vaporization

To determine the magnesium source concentration we assume that the vapor concentration is essentially equal to that given by the equilibrium vapor pressure of magnesium at the temperature of the crucible. It has been brought to our attention that the evaporation rates may be far from equilibrium, especially for high molecular weight species evaporating into low molecular weight gases.[14] Since these rates may have a dramatic effect on our results, we have performed a series of very simple experiments to check the validity of this assumption.

Since the magnesium vapor is seen to be constrained to a plume, the evaporation rate can be closely modeled by

$$\dot{m} = \rho_{mg}\bar{V}S_x, \tag{12}$$

where $\dot{m}$ is the magnesium mass loss rate, ρ_{mg} is the density of magnesium, $\bar{V}$ is the average velocity of the plume, and S_x is the cross sectional area of the plume at the point where the magnesium condenses. This equation may be rearranged to

$$\rho_{mg} = \frac{\dot{m}}{\bar{V}S_x}. \tag{13}$$

It is assumed that the diameter of the condensing plume is equal to the inside diameter of the crucible and therefore is 2.19 cm. From numerical modeling of the convective flows and temperature profiles within the experimental apparatus it is estimated that the average velocity above the crucible at the point where the magnesium condenses is approximately 30 cm s^{-1}. We estimate that this value may be as small as 10 or as high as 50 cm s^{-1} and its value is the most debatable quantity in Eq. (13).

By measuring the mass loss rate under constant conditions, the density of magnesium vapor above the crucible can be estimated. This magnesium density can then be converted to a pressure in Torr, assuming that the hydrogen carrier gas behaves ideally.

The results of four evaporation runs are shown in Table II. Before an experiment, a crucible containing the magnesium sample was weighed. After the experiment, the crucible and remainder of the sample was re-weighed to determine the amount of magnesium lost during the test. During a run, the crucible temperature was maintained constant and the run was sufficiently long that the heat up/cool down tran-

sient period were a small fraction of the total experimental run time. The elapsed times shown in Table II do not include these transient periods.

Column 6 of Table II gives the magnesium vapor pressure calculated via these evaporation experiments. The equilibrium vapor pressure calculated using Eq. (3) is given in the column labeled equilibrium vapor pressure and the ratio of the experimental vs calculated vapor pressures is given in the last column. The results are fairly consistent and in general it appears that the evaporation experiments yield a magnesium vapor pressure which is roughly one half of that based on published equilibrium vapor pressure equations.

If the magnesium concentration is in reality about a factor of two lower in our experiments than we have assumed in our data reduction then this would lower the data points in Fig. 6 by a constant value, $(\ln 2)^{2/3} \approx 0.78$. Eq. (6) would then be modified to yield

$$(\ln S)^{2/3} = 2405/T - 1.81. \tag{14}$$

The magnesium critical temperature calculated from Eq. (14) is then only 1329 K. We also note that the intercept (-1.81) lies well below the range of values $(-1.06$ to $-1.71)$ expected for this quantity.[9]

In view of the assumptions used in back-calculating the magnesium vapor pressure from our mass-loss data, we feel that the published vapor pressure curves originally used to reduce our nucleation data are at least reasonable and lend confidence to our assumption that the magnesium concentration at the nucleation front is approximately equal to the equilibrium vapor pressure in the crucible. The magnitude of the final ratio in column 6 of Table II is fairly sensitive to the choice of the average plume velocity. For example, if we had chosen an average plume velocity of 15 cm s^{-1}, (which is within the 10–50 cm s^{-1} range we estimate for this quantity), rather than a value of 30 cm s^{-1}, we would have nearly perfect agreement between our mass loss data and the equilibrium predictions. Similarly, had we chosen a value of 10 cm s^{-1} our mass loss experiments would lead to magnesium partial pressures ~50% greater than equilibrium. Because of this sensitivity to an assumed quantity our only real conclusion from these simple experiments is that the evaporation rates are fairly consistent with our expectations from Eq. (3) over the temperature and pressure ranges used in this work. Based on these results we feel that the actual evaporation rate is not significantly lower than equilibrium predictions, although our supersaturation data, as reported, should probably be regarded as upper limit values.

IV. CONCLUSIONS

We have completed a study of magnesium nucleation over the temperature range from 700 to 950 K. Data was taken at both 100 and 250 Torr ambient pressure and the results are indistinguishable. The data do not seem to follow the predictions of Classical Nucleation Theory. Application of the theory to our data yields unrealistically low fluxes which cannot be explained even by considering the possibility of very large errors in our data. It should be noted that our data and Classical Nucleation Theory can be brought into agreement by using a value for the surface tension which is roughly 60% of the literature value for magnesium at the melting point.

Application of Scaled Nucleation Theory yields reasonable and fairly consistent values for the magnesium critical temperature and critical cluster size. Also, using our data and Scaled Nucleation Theory we are able to estimate an effective surface tension for the growing magnesium clusters. Interestingly, if this effective surface tension information is used in the Classical expression, our temperature and supersaturation data yield reasonable values for the condensation flux. Although in general most of the results of Scaled Theory are reasonable, other quantities such as the excess surface entropy per molecule appear to be on the limits of the predictions of the theory. It is possible that such a low value may be due to some type of symmetry or order in the developing cluster nucleus.

It is clear that additional refractory nucleation studies are necessary to resolve these and other discrepancies between data and theory. It is also clear that reliable vapor pressure curves for refractory metals are needed in order to understand the behavior of metallic vapors at high temperature.

ACKNOWLEDGMENTS

[1] J. S. Mathis, Annu. Rev. Astron. Astrophys. **28**, 37 (1990).
[2] J. R. Stephens and S. H. Bauer, in *Proceedings of the 13th International Symposium on Shock Tubes and Waves* (State University of New York, Albany, New York, 1982).
[3] D. J. Frurip and S. H. Bauer, J. Phys. Chem. **81**, 1001 (1977).
[4] J. A. Nuth, K. A. Donnelly, B. Donn, and L. U. Lilleleht, J. Chem. Phys. **85**, 1116 (1986).
[5] J. A. Nuth and B. Donn, J. Chem. Phys. **77**, 2639 (1982).
[6] G.-S. Cha, H. Uchtmann, J. A. Fisk, and J. L. Katz, J. Chem. Phys. **101**, 459 (1994).
[7] R. Becker and W. Döring, Ann. Phys. **24**, 719 (1935).
[8] J. Lothe and G. M. Pound, J. Chem. Phys. **36**, 2080 (1962).
[9] J. A. Nuth III and F. T. Ferguson, *Nuclear and Crystallographic Liquids and Glasses* **30**, 23 (1993).
[10] B. Hale, Phys. Rev. A **33**, 4156 (1986).
[11] B. Hale, P. Kemper, and J. A. Nuth III, J. Chem. Phys. **91**, 4314 (1989).
[12] *Metals Reference Book*, 3rd ed., Vol. II (Butterworth, Washington, DC, 1962).
[13] *Metals Handbook, Desk Edition* (The American Society for Metals, Metals Park, Ohio, 1985).
[14] S. H. Bauer (personal communication).